ORGANIC LETTERS

2008
Vol. 10, No. 11
2167−2170

Triaryl(1-pyrenyl)bismuthonium Salts: Efficient Photoinitiators for Cationic Polymerization of Oxiranes and a Vinyl Ether

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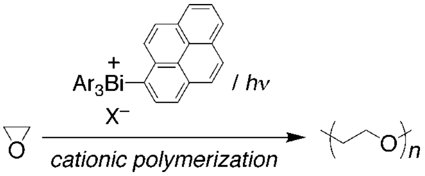
Received March 10, 2008

ABSTRACT



Photoirradiation of triaryl(1-pyrenyl)bismuthonium salts in acetonitrile afforded triarylbismuthanes and pyrene, accompanied by the generation of protic acids. Triaryl(1-pyrenyl)bismuthonium hexafluoroantimonates have proven to behave as efficient photoinitiators for cationic polymerization of oxiranes and a vinyl ether, affording the corresponding polymers in good yields within 1 min.

Photoinduced cationic polymerization has long been the subject of considerable interest in the fields of polymer and materials chemistry.[1] The efficiency of the polymerization processes relies heavily on the reactivity of photoinitiators, which play a crucial role in generating proton or Lewis acids via photodecomposition. Onium-type compounds derived from the group 16 and 17 elements such as sulfur(IV)[2] and iodine(III)[3] have been widely used as cationic photoinitiators. Typically, sulfonium and iodonium salts bearing aryl substituents are excited directly or indirectly by UV−vis light to undergo the E−C bond homolysis (E = S, I). It is believed that highly reactive S(III) and I(II) intermediates abstract hydrogen from the reaction media (monomers and/or solvents) followed by reductive elimination of R_nE species (E = S, $n = 2$; E = I, $n = 1$). As a consequence, the abstracted hydrogen is formally oxidized to proton, which initiates the cationic polymerization of electron-rich monomers such as oxiranes and vinyl ethers.

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(1) For example, see: (a) Crivello, J. V. *Adv. Polym. Sci.* **1984**, *62*, 1–48. (b) Dietliker, K. In *Chemistry and Technology of UV and EB Formulation for Coatings, Inks, and Paints*; Oldring, P. K. T., Ed.; SITA Technology: London, 1991; Vol. 3, pp 329−477. (c) Pappas, S. P. *Photopolym. Photoimaging Sci. Technol.* **1989**, 55–73. (d) Lazauskaite, R.; Grazulevicius, J. V. *Handbook Photochem. Photobiol.* **2003**, *2*, 335–392. (e) Crivello, J. V.; Ma, J.; Jiang, F.; Hua, H.; Ahn, J.; Ortiz, R. A. *Macromol. Symp.* **2004**, *215*, 165–177. (f) Yagci, Y. *Macromol. Symp.* **2004**, *215*, 267–280. (g) Yagci, Y. *Macromol. Symp.* **2006**, *240*, 93–101.

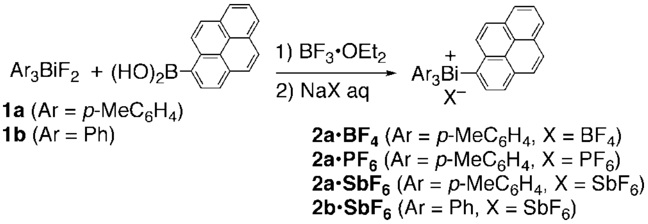
(2) For example, see: (a) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci.: Polym. Chem. Ed.* **1979**, *17*, 977–999. (b) Crivello, J. V.; Lee, J. L. *Macromolecules* **1981**, *14*, 1141–1147. (c) Crivello, J. V.; Lee, J. L. *Macromolecules* **1983**, *16*, 864–870. (d) Crivello, J. V.; Kong, S. *Macromolecules* **2000**, *33*, 833–842. (e) Crivello, J. V.; Kong, S. *Macromolecules* **2000**, *33*, 825–832. (f) Zhou, W.; Kuebler, S. M.; Carrig, D.; Perry, J. W.; Marder, S. R. *J. Am. Chem. Soc.* **2002**, *124*, 1897–1901. (g) Pappas, S. P.; Tilley, M. G.; Pappas, B. C. *J. Photochem. Photobiol., A* **2003**, *159*, 161–171. (h) Crivello, J. V.; Falk, B.; Zonca, M. R., Jr *J. Appl. Polym. Sci.* **2004**, *92*, 3303–3319. (i) Crivello, J. V.; Bulut, U. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 6750–6764.

10.1021/ol8005453 CCC: $40.75 © 2008 American Chemical Society
Published on Web 05/06/2008

It is known that the dissociation energy of a Bi−C covalent bond (143 kJ mol^{-1}) is much smaller than that of S−C (272 kJ mol^{-1}) and I−C bonds (213 kJ mol^{-1}).[4] Furthermore, organobismuth(V) compounds possess high oxidizing ability due to the facile Bi(V)/Bi(III) redox process.[5] These characteristic properties of bismuth are beneficial for designing a new class of efficient cationic photoinitiators. To our knowledge, however, no attempt has been made to use the bismuth(V)-based photoinitiators in UV−vis curing systems. Herein, we report the first example of photoinitiated cationic polymerization of oxiranes and a vinyl ether using the onium-type bismuth(V) compounds.

To use the intense light of 365 nm emitted from Hg arc lamp, we designed triaryl(1-pyrenyl)bismuthonium salts (**2·X**), which bear a photoactive pyrene unit as the Bi substituent. The target compounds **2·X** were easily prepared by the BF_3-promoted metathesis reaction of triarylbismuth difluorides (**1a**,**b**) with 1-pyrenylboronic acid according to a previously established procedure (Scheme 1)[6] and characterized by ^{1}H NMR, IR, MS, and elemental analysis. In the IR spectra of **2·X**, strong absorptions due to the counteranions, BF_4^-, PF_6^-, and SbF_6^-, were observed at ν 1150−900 cm^{-1} (BF_4^-), 900−700 cm^{-1} (PF_6^-), and 656−659 cm^{-1} (SbF_6^-). In the MS spectra, intense peaks assignable to $[Ar_3Bi(1\text{-pyrenyl})]^+$ ions were detected at *m*/*z* 641 (Ar = Ph) and 683 (Ar = *p*-MeC_6H_4). The structures of **2a·BF$_4$** and **2a·SbF$_6$** were further elucidated by X-ray crystallography.[7] Single crystals of these compounds were grown from CH_2Cl_2−Et_2O. As shown in Figure 1, each bismuth center adopts a distorted tetrahedral geometry with C−Bi−C bond angles and Bi−C bond lengths of 103.6(2)−113.3(2)° and 2.189(6)−2.198(6) Å for **2a·BF$_4$** and 106.9(2)−111.5(2)° and 2.179(5)−2.187(5) Å for **2a·SbF$_6$**. In both compounds, the counteranions are apart from the bismuth center, suggesting that **2a·X** have an onium nature intrinsically.[8]

Scheme 1. Synthesis of Triaryl(1-pyrenyl)bismuthonium Salts



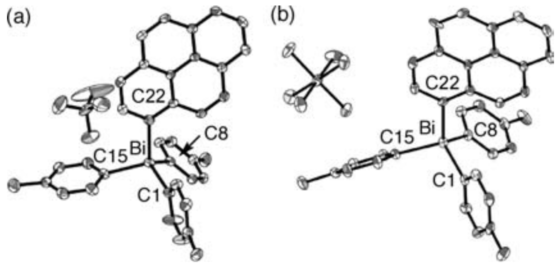


Figure 1. ORTEP diagrams (30% probability ellipsoids) of (a) **2a·BF$_4$** and (b) **2a·SbF$_6$**. Selected bond lengths (Å) and angles (deg). **2a·BF$_4$**: Bi−C1, 2.189(6); Bi−C8 2.198(6); Bi−C15, 2.192(6); Bi−C22, 2.193(6); C1−Bi−C8, 113.3(2); C1−Bi−C15, 106.9(2); C1−Bi−C22, 112.0(2); C8−Bi−C15, 113.2(2); C8−Bi−C22, 107.4(2); C15−Bi−C22, 103.6(2). **2a·SbF$_6$**: Bi−C1, 2.187(5); Bi−C8 2.179(5); Bi−C15, 2.181(6); Bi−C22, 2.185(4); C1−Bi−C8, 108.5(2); C1−Bi−C15, 111.5(2); C1−Bi−C22, 111.14(19); C8−Bi−C15, 108.6(2); C8−Bi−C22, 110.1(2); C15−Bi−C22, 106.9(2).

The UV−vis absorption spectrum of **2a·BF$_4$** showed rather broad pyrene-derived $\pi-\pi^*$ transitions at longer wavelengths as compared to those of unsubstituted pyrene (Figure 2). The fluorescence spectrum of **2a·BF$_4$** exhibited the broad, structureless emission at around 370−500 nm (λ_{ex} = 334

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(3) For example, see: (a) Crivello, J. V.; Lam, J. H. W. *Macromolecules* **1977**, *10*, 1307–1315. (b) Muneer, R.; Nalli, T. W. *Macromolecules* **1998**, *31*, 7976–7979. (c) Yagci, Y.; Hepuzer, Y. *Macromolecules* **1999**, *32*, 6367–6370. (d) Hartwig, A.; Harder, A.; Lühring, A.; Schröder, H. *Eur. Polym. J.* **2001**, *37*, 1449–1455. (e) Sipani, V.; Scranton, A. B. *J. Photochem. Photobiol., A* **2003**, *159*, 189–195. (f) Yonet, N.; Yagci, Y.; Ochiai, B.; Endo, T. *Macromolecules* **2003**, *36*, 9257–9259. (g) Andruleviciute, V.; Lazauskaite, R.; Grigalevicius, S.; Grazulevicius, J. V. *Eur. Polym. J.* **2006**, *42*, 1069–1074. (h) Crivello, J. V.; Bulut, U. *Macromol. Symp.* **2006**, *240*, 1–11.

(4) Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: Oxford, 1998.

(5) For example, see: (a) Challenger, F.; Richards, O. V. *J. Chem. Soc.* **1934**, 405–411. (b) Barton, D. H. R.; Kitchin, J. P.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1978**, 1099–1100. (c) Barton, D. H. R.; Lester, D. J.; Motherwell, W. B.; Papoula, M. T. B. *J. Chem. Soc., Chem. Commun.* **1979**, 705–707. (d) Dodonov, V. A.; Zinov'eva, T. I.; Osadchaya, N. N. *Zh. Obshch. Khim.* **1988**, *58*, 712. (e) Matano, Y.; Nomura, H. *J. Am. Chem. Soc.* **2001**, *123*, 6443–6444. (f) Matano, Y.; Nomura, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3028–3031. (g) Mitsumoto, Y.; Nitta, M. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1029–1034. (h) Matano, Y.; Hisanaga, T.; Yamada, H.; Kusakabe, S.; Nomura, H.; Imahori, H. *J. Org. Chem.* **2004**, *69*, 8676–8680. (i) Matano, Y.; Suzuki, T.; Shinokura, T.; Imahori, H. *Tetrahedron Lett.* **2007**, *48*, 2885–2888.

(6) (a) Matano, Y.; Begum, S. A.; Miyamatsu, T.; Suzuki, H. *Organometallics* **1998**, *17*, 4332–4334. (b) Matano, Y.; Begum, S. A.; Miyamatsu, T.; Suzuki, H. *Organometallics* **1999**, *18*, 5668–5681, Typical procedure: To a CH_2Cl_2 solution (10 mL) containing **1a** (0.52 g, 1.0 mmol) and 1-pyrenylboronic acid (0.27 g, 1.1 mmol) was added $BF_3·OEt_2$ (0.23 mL, 2.0 mmol) at 0 °C, and the mixture was stirred for 2 h at room temperature. An aqueous solution of $NaSbF_6$ (5.2 g, 20 mmol) was then added, and the resulting two-phase solution was vigorously stirred for 20 min. The aqueous phase was separated and extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$, passed through a short silica gel column, and evaporated under reduced pressure to leave a solid residue, which was recrystallized from CH_2Cl_2−Et_2O to afford **2a·SbF$_6$** (0.87 g, 95%) as a pale yellow solid. Bismuthonium salts **2·X** are thermally stable (Mp ≥ 176 °C) and can be kept as a solid state for more than 1 year in the dark.

(7) **2a·BF$_4$**: $C_{37}H_{30}BBiF_4$, monoclinic, $P2_1/c$, a = 9.779(3) Å, b = 19.034(5) Å, c = 16.871(5) Å, β = 102.501(1)°, V = 3065.8(15) Å^3, Z = 4, D_c = 1.669 g cm^{-3}, 6979 independent, 389 variables, R = 0.0545 ($I > 2.00\sigma(I)$), $_wR$ = 0.1021, GOF = 1.041. **2a·SbF$_6$**: $C_{37}H_{30}BiF_6Sb$, triclinic, $P\bar{1}$, a = 9.309(3) Å, b = 12.507(4) Å, c = 14.931(5) Å, α = 80.043(12)°, β = 80.653(13)°, γ = 73.665(12)°, V = 1631.1(10) Å^3, Z = 2, D_c = 1.872 g cm^{-3}, 7093 independent, 407 variables, R = 0.0408 ($I > 2.00\sigma(I)$), $_wR$ = 0.0743, GOF = 1.039.

(8) The distances between the bismuth and the nearest fluorine atoms are 4.4−4.5 Å.

(9) λ_{max}/nm ($\epsilon/10^2$ M^{-1} cm^{-1}) of **2a·X** in CH_2Cl_2: **2a·BF$_4$** [341 (260), 352 (290), 358 (270), 377 (88)]; **2a·PF$_6$** [342 (250), 352 (290), 358 (280), 377 (89)]; **2a·SbF$_6$** [342 (270), 352 (310), 358 (300), 377 (96)].

(10) Fluorescence quantum yields of **2a·BF$_4$**, **2a·PF$_6$**, and **2a·SbF$_6$** in CH_2Cl_2 were determined as 0.04, 0.02, and 0.02, respectively, by comparison with that of pyrene (0.38) in the same solvent: Karpovich, D. S.; Blanchard, G. J. *J. Phys. Chem.* **1995**, *99*, 3951–3958.

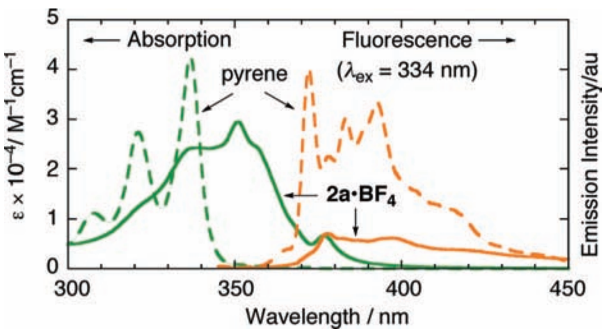


Figure 2. UV−vis absorption (green) and fluorescence (orange) spectra of **2a·BF$_4$** (solid line) and pyrene (dashed line) in CH_2Cl_2.

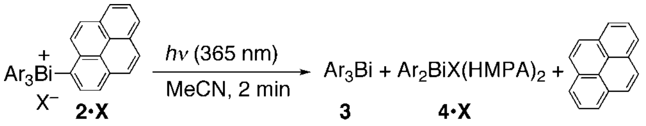
nm), whose intensity is considerably smaller than that of pyrene. It was found that the absorption and emission maxima of **2a·X** in CH_2Cl_2 are little affected by the counteranions (**X**).[9] The relatively low fluorescence quantum yields of **2a·X** may be due in a part to the heavy-atom effect of the triarylbismuthonio group.[10]

We next examined the photochemical reaction of **2·X** in acetonitrile under several conditions (Table 1). Irradiation of an acetonitrile solution of **2a·BF$_4$** (0.01 M) with a high-pressure Hg arc lamp (I > 150 mW cm^{-2}) through an aqueous $CuSO_4$ filter (λ_{irr} > 320 nm) for 2 min afforded tri(*p*-tolyl)bismuthane (**3a**) and pyrene in 30% and 70% yields, respectively, together with insoluble substances (entry 1). When the reaction was carried out in the presence of excess hexamethylphosphoramide (HMPA), di(*p*-tolyl)bismuth tetrafluoroborate−HMPA complex (**4a·BF$_4$**) was formed in 65% yield together with **3a** (25%) and pyrene (75%) (entry 2). These results suggest that fluoroboric acid is generated by photodecomposition of **2a·BF$_4$** in solution.[11] Indeed, when the solution of **2a·BF$_4$** was irradiated in the presence of 2,6-di(*tert*-butyl)-4-methylpyridine, the corresponding pyridinium salt was produced in 90% yield based on the bismuthonium salt (entry 3). Under this condition, the yield of **3a** increased to 70%, which implies the pyridine acts as a proton scavenger to suppress the acidolysis of the Bi−C bond of **3a**. Other bismuthonium salts **2a·PF$_6$**, **2a·SbF$_6$**, and **2b·SbF$_6$** also decomposed photochemically to give Bi(III) compounds and pyrene, accompanied by generation of the respective protic acids (entries 4−6). Quantum yields of the photodecomposition (Φ_{dec}) of **2a·X** in acetonitrile were determined by chemical actinometry using a potassium ferrioxalate[12] to be 0.20−0.22, which are comparable to those reported for triarylsulfonium salts and diaryliodonium salts (Φ_{dec} = 0.17−0.22).[2a,3a] It should be noted that the efficiency of photodecomposition of **2·X** does not depend on the nature of counteranions (*vide infra*).

Scheme 2 illustrates a possible mechanism for the generation and reactions of protic acids in the present Bi(V) system. A part of the excited bismuthonium salt **2·X** undergoes homolysis of the Bi−C(pyrenyl) bond to generate a Bi(IV) radical cation and a pyrenyl radical (Scheme 2, eq 1). Presumably, the $\pi-\pi^*$ transition of the pyrenyl moiety of **2·X** weakens the Bi−C(pyrenyl) bond selectively. The Bi(IV) radical cation thus generated should be highly reactive and promptly generate a protic acid (H^+X^-) via hydrogen abstraction or proton-coupled electron transfer with the reaction media followed by reductive elimination of triarylbismuthane **3** (Scheme 2, eq 2), and the pyrenyl radical is likely to abstract a hydrogen from the media to afford pyrene (Scheme 2, eq 3). The added pyridine quenches the proton to give a pyridinium salt (Scheme 2, eq 4). While, in the absence of a base, the proton cleaves the Bi−C bonds of **3** to give Ar_2Bi^+ species, which can be trapped as HMPA complexes **4** (Scheme 2, eq 5).

Encouraged by the above results, we evaluated the photoinitiating ability of the 1-pyrenylbismuthonium salts **2·X** for cationic polymerization of some oxiranes **5**−**7** and vinyl ether **8** (Table 2). In the absence of **2a·SbF$_6$** or in the dark, cyclohexene oxide (**5**) did not polymerize at all (entries 1 and 2). In sharp contrast, the cationic polymerization of **5** took place in the presence of 0.1 mol % of **2a·SbF$_6$** or **2a·PF$_6$** under photoirradiation (365 nm) for 1

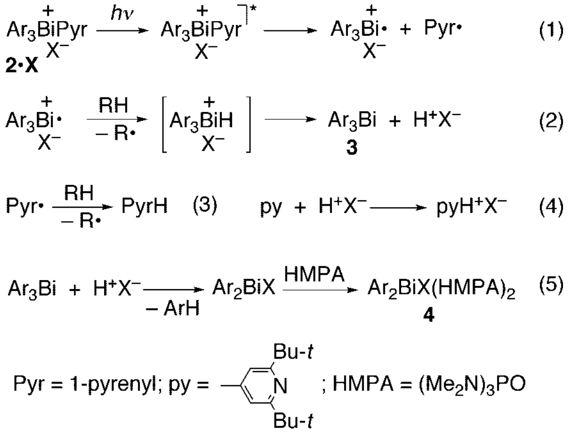
Table 1. Photochemical Reaction of **2·X** in Acetonitrile[a,b]



entry	2a·X	Φ_{dec}	additive	products (NMR yield/%)[c]
1	**2a·BF$_4$**	ND[d]	none	**3a** (30), pyrene (70)[e]
2	**2a·BF$_4$**	0.20	HMPA	**3a** (25), **4a·BF$_4$** (65), pyrene (75)
3	**2a·BF$_4$**	ND[d]	py[f]	**3a** (70), pyrene (ND), $pyH^+BF_4^-$ (90)[f]
4	**2a·PF$_6$**	0.22	HMPA	**3a** (20), **4a·PF$_6$** (65), pyrene (80)
5	**2a·SbF$_6$**	0.22	HMPA	**3a** (25), **4a·SbF$_6$** (70), pyrene (80)
6	**2b·SbF$_6$**	0.22	HMPA	**3b** (20), **4b·SbF$_6$** (70), pyrene (80)

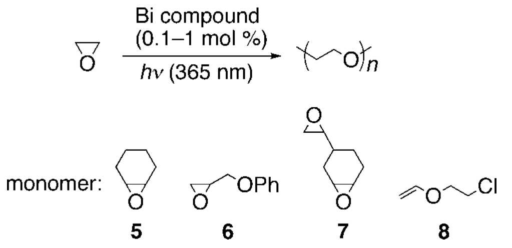
[a] The photoirradiation was carried out with a high-pressure Hg arc lamp through an aqueous $CuSO_4$ filter at room temperature. [b] **a**: Ar = *p*-MeC_6H_4. **b**: Ar = Ph. [c] Determined by ^1H NMR using an internal standard (1,1,2,2-tetrachloroethane). [d] Not determined. [e] Insoluble substances were formed. [f] py = 2,6-di(*tert*-butyl)-4-methylpyridine.

Scheme 2. Possible Mechanism for Photodecomposition of **2·X**



min to give poly(cyclohexene oxide) (**5P**) (entries 3 and 4), indicating that both photoirradiation and initiators (**2X**) are necessary to polymerize **5**. The M_n and M_w/M_n (M_w = weight-average molecular weight; M_n = number-average molecular weight) of **5P** were determined by means of gel permeation chromatography (GPC) using PEG as a standard to be 8900−9500 and 1.3−1.2, respectively. The isolated yield of **5P** was found to depend on the counteranion: **2a·SbF$_6$** gave a better result than **2a·PF$_6$** (vide infra). Prolonged irradiation improved the yield of **5P** only slightly (entry 5), suggesting that the bismuthonium salt was consumed within a minute under the reaction conditions employed. Increasing the amount of **2a·PF$_6$** did not improve the yield of **5P** dramatically (entry 6), partly due to its insufficient solubility in **5**. When **2a·BF$_4$** was used as the initiator, polymerization of **5** did not proceed efficiently (entries 7 and 8). It should be emphasized again that Φ_{dec} of **2·X** do not depend on the nature of counteranions. These results imply that the efficiency of the cationic polymerization of **5** is deeply related to the nucleophilicity of the counteranions of **2a·X**. That is, less nucleophilic anion is better for stabilizing the carbenium ion intermediates generated in the chain-propagating step, as was observed for the cationic polymerizations initiated by triarylsulfonium and diaryliodonium salts.[2,3] The phenyl derivative **2b·SbF$_6$** also initiated the polymerization of **5** with almost the same efficiency (entry 9). By contrast, triphenylbismuthane (**3b**), which does not absorb the light of 365 nm, did not initiate the polymerization of **5** under the same conditions (entry 10). The photoinitiated cationic polymerizations of oxiranes **6** and **7** and vinyl ether **8** were also achieved by using 0.1−0.5 mol % of **2a·SbF$_6$**, yielding the corresponding polymers in 48−90% yields (entries 11−15).

Table 2. Photoinduced Cationic Polymerization Using **2·X**[a]



entry	initiator (mol %)	monomer	time	yield/%[b]	M_n (M_w/M_n)[c]
1	none	**5**	1 min	NR[d]	– (–)
2	**2a·SbF$_6$** (0.1)	**5**	1 h[e]	NR[d]	– (–)
3	**2a·SbF$_6$** (0.1)	**5**	1 min	88	9500 (1.2)
4	**2a·PF$_6$** (0.1)	**5**	1 min	41	8900 (1.3)
5	**2a·PF$_6$** (0.1)	**5**	3 min	46	9000 (1.3)
6	**2a·PF$_6$** (1)	**5**	1 min	58	8500 (1.4)
7	**2a·BF$_4$** (0.1)	**5**	1 min	<1	ND (ND)[f]
8	**2a·BF$_4$** (1)	**5**	3 min	<1	ND (ND)[f]
9	**2b·SbF$_6$** (0.1)	**5**	1 min	80	9000 (1.2)
10	**3b** (0.1)	**5**	1 min	NR[d]	– (–)
11	**2a·SbF$_6$** (0.1)	**6**	1 min[g]	48	7800 (1.2)
12	**2a·SbF$_6$** (0.5)	**6**	1 min[g]	59	8400 (1.2)
13	**2a·SbF$_6$** (0.1)	**7**	1 min	90	15800 (1.4)
14	**2b·SbF$_6$** (0.1)	**7**	1 min	85	16100 (1.4)
15	**2a·SbF$_6$** (0.1)	**8**	1 min	74	16600 (1.7)

[a] The photoirradiation was carried out with a high pressure Hg arc lamp through an aqueous $CuSO_4$ filter at room temperature. [b] Isolated yields of polymers after reprecipitation. [c] M_n and M_w were determined by GPC (JAIGEL-5H-AF, eluted with $CHCl_3$) using poly(ethylene glycol) as a standard. [d] No reaction. [e] No irradiation. [f] Not determined. [g] After irradiation, the reaction mixture was stood in the dark for 30 min.

In summary, we have demonstrated for the first time that triaryl(1-pyrenyl)bismuthonium salts photoinitiate the cationic polymerization of electron-rich monomers by using UV−vis light. It is likely that the Bi(IV) radical cation, generated by the selective Bi−C(pyrenyl) bond cleavage, formally oxidizes hydrogen ($H^•$) to proton (H^+) via the facile Bi(IV)/Bi(III) redox process. The efficiency of polymerization relies on nucleophilicity of the counteranions of the bismuthonium salts, and the hexafluoroantimonate has proven to exhibit the highest polymerizing ability. As we can introduce a wide range of chromophores onto the bismuth center of bismuthonium salts, the onium-type Bi(V) compounds will be highly promising candidates as efficient photoinitiators for cationic polymerization.

Acknowledgment. This work was supported by a Grant-in-Aid (No. 17350018) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: Experimental details, spectral and analytical data of **2·X** and CIF files for **2a·BF$_4$** and **2a·SbF$_6$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) It is known that the Bi−C bonds of triarylbismuthanes (Ar_3Bi) are readily cleaved by 1 equiv of strong protic acids (HX) to give cationic diarylbismuth(III) species (Ar_2BiX) which are apt to transform into insoluble polymeric substances. In the presence of excess HMPA, however, the cationic species can be isolated as soluble HMPA complexes of the type $Ar_2BiX(HMPA)_2$. For example, see: (a) Carmalt, C. J.; Norman, N. C.; Orpen, A. G.; Stratford, S. E. *J. Organomet. Chem.* **1993**, *460*, C22–C24. (b) Matano, Y.; Miyamatsu, T.; Suzuki, H. *Organometallics* **1996**, *15*, 1951–1953.

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